BIOSORPTION OF METHYLENE BLUE FROM AQUEOUS SOLUTION USING DRIED WATER HYACINTH *(Eichornia crassipes)*

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A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

MAY 2009

DECLARATION

I declare that this thesis entitled "biosorption of methylene blue from aqueous solution using dried water hyacinth *(Eichornia crassipes*)" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree."

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DEDICATION

Special dedication to my beloved, Syahid for his never lack of love, kindness, supports and motivations, also to both my parents for their prayers and inspirations, my supervisor, my fellow friends, and everyone involved.

For all your love and care, I thank you and overwhelmed with gratitude.

ACKNOWLEDGEMENT

Praise be to Allah S.W.T for his help and guidance that finally I am able to complete this undergraduate research project as one of my requirement to complete my study.

First and foremost I would like to extend my deepest gratitude to all the parties involved in this research. A special thank you to my supervisor Mdm. Jun Haslinda binti Haji Shariffuddin for her time and dedications in guiding me throughout the research work right from the beginning until the end of it. All her advices and comments are most precious and bring nothing but perfection to the outcome of this research project.

Also, a thousand of appreciation to all my lecturers in the Faculty of Chemical and Natural Resources Engineering (FKKSA), for their help and support during this project development.

Not forgetting, to all my fellow friends, thank you for believing in me and helping me through the difficult times. The knowledge and experiences I gained along the process of completing this project would prove to be invaluable for the better to guide me for the challenges that lies ahead. And last but never the least to all my family members, I can never thank you enough for your love and prayers, and supporting me throughout my studies in University Malaysia Pahang.

ABSTRACT

In this study, dried water hyacinth (DWH), an abundant and freely available plant is proposed as a biosorbent for the biosorption of Methylene Blue (MB) dye from aqueous solutions. The effects of the biosorbent dosage, initial concentration, pH and contact time were studied in a batch experiments at room temperature (± 27^{o}C). Results show that the optimum condition is at 0.55g, 80 mg/L, pH 7.0 and 90 minutes of contact time, respectively. The functional group on the DWH surface is analyzed as well to observe the availability of binding sites for the sorption. Samples of MB after the uptake are analyzed with UV-Vis spectrophotometer. Langmuir adsorption isotherm model is used for the mathematical description to describe the biosorption equilibrium process and the maximum sorption capacity is determined to be 19.61 mg/g. The study is economically feasible and it is proven to be favorable. Also, water hyacinth is a potentially plant to be an effective biosorbent for the uptake of MB.

ABSTRAK

Keupayaan keladi bunting, tumbuhan akuatik terbiar dan mudah diperoleh telah dikaji sebagai agen bio-penjerap dalam memisahkan atau menjerap pewarna *Methylene Blue* dari larutan dalam skala makmal. Pengaruh jumlah dos agen bio-penjerap, kepekatan awal larutan pewarna, pH dan masa telah dikaji dalam eksperimen ini. Data paling optima yang diperolehi adalah 0.55 g, 80 mg/L, pH 7.0 dan 90 minit penggunaan, setiap satu. Kesemua kepekatan akhir larutan dianalisa menggunakan UV-Vis Spectrophotometer. Langmuir model telah dipilih untuk menerangkan proses penjerapan dari segi pengiraan matematik dan nilai jerapan maksima adalah 19.61 mg/g. Kajian ini telah terbukti bahawa penggunaan serbuk keladi bunting sebagai agen bio-penjerap adalah efektif dari segi ekonomi dan penggunaannya.

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DWH -	Dried water hyacinth
MB -	Methylene blue
Pb -	Lead
Cd -	Cadmium
U -	Uranium
Cu -	Copper
Zn -	Zinc
Cr -	Chromium

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Dyes are extensively used in many industries including printing processes, textile, plastics, cosmetics, etc. to add color for their final products. Most of the unspent dyes generate undesirable effluents and usually will be discharged to the environment with or without treatment. There are over 100,000 available dyes with more than 7 x 105 tonnes of dyestuff produced annually (X.S. Wang et al., 2008). Approximately 2% of dyes produced are discharged in effluent from manufacturing operations while 10% are discharged in effluent from textile and associated industries (X.S. Wang et al., 2008). The textile industry contributes about 22% of the total volume of industrial wastewater generated in the country (B.H. Hameed et al., 2008). The release of dyes into waters by industries is undesirable and causes serious environmental problems. It contains various organic compounds and toxic substances which are hazardous and harmful to aquatic organisms. The colored waste water in the receiving streams reduces the light penetration through the water's surface and therefore, reduces photosynthesis activity (Weisburger, 2002).

There are several techniques of removal of dyes from waste water. Some of them are, by flotation, precipitation, oxidation, filtration, coagulation, ozonation, supported liquid membrane, and also biological process (A.S. Mahmoud et al., 2007). Meanwhile, a new and more environmental friendly method, the biosorption process is proven to be a promising process to remove dyes from effluent. It is stated by D.J Ju et al. in his research on 2006, biosorption is also known as the uptake or accumulation of chemicals by biomass. This process is similar to adsorbent process which it is cost-effective, easy to operate, simply designed and insensitivity to toxic substances. In this study, Methylene Blue (MB), known as strong adsorptions into solid, will be used as the biosorbate. MB is an important basic dye widely used for printing cotton and tannin, and dyeing leather. Even though it is not strongly hazardous, MB can cause harmful effects to human and other living organisms. Too much exposed of MB can cause eye burns and causes irritation to the skin.

Activated carbon is well known as the most widely used adsorbent and proven to be effective for removal of dye due to its large surface area, micro-porous structure, high adsorption capacity, etc, (X.S. Wang et al., 2008) but since it is high cost, this limits its usage in large scale production. Therefore, researches have investigated other alternatives adsorbent which is cost-effective, efficient and easily available materials for the biosorption process. Some of the proven efficiently adsorbent materials are *Posidonia Oceanica* (L.) fibre (M.C. Ncibi et al., 2007), orange and banana peels (Annadurai et al., 2002), peanut hull (Gong et al., 2005) and, pumpkin seed hull (B.H. Hameed et al., 2007). In this study, dried water hyacinth (DWH), an agricultural solid waste, is used as an alternative low-cost dye adsorbent. The water hyacinth is a relatively high growth rate plant and when uncontrolled, it can disturb the aquatic ecosystem equilibrium, thus inducing environmental damages (R. Bodo et al., 2004). To make better use of this cheap and abundant agricultural resource plant, it is used as an adsorbent to remove Methylene Blue from aqueous solutions.

1.2 Problem Statement

The expose of dyes into environment by various industries has been aesthetically undesirable and too much of it will eventually cause serious environmental effect, aquatic or non-aquatic. This is due to its properties which are mostly toxic, mutagenic, and carcinogenic (B.H. Hameed et al., 2008). Dyes are causing pollution to the environment, for example, dyes adsorb and reflect sunlight from entering water and thus interfere the aquatic ecosystem. Dyes when release can have acute and/or chronic effects (X.S. Wang et al., 2008). It is evidently, therefore, investigating the removal of dyes is significant environmental, technical, and commercially important.

Water hyacinth is a free-floating aquatic weed originating from tropical areas in so many countries. It is naturally a rapid and uncontrollable growth plant, thus it has become a major cause of water irrigation especially during raining season, where it can be found blocking the drains and water sources. It has caused high costs and labour requirements to control the plant, leaving only temporary removal of the water hyacinths and abundantly growing. This resulted in a major massive growth of mosquito’s pest which will lead to serious health problems to the society. Therefore, in making this plant a better use, it is proposed as a biosorbent to remove dyes.

For this study purpose, the water hyacinth is better to be used in dried condition. This is because, in living condition, the plant needs a huge and somehow massive area for maintaining its growth. Therefore, it is better to dry the water hyacinth for it is more user-friendly and will maximize the place of work instead of place to grow the plant. Also, dried water hyacinth can lessen the usage of transportation and also reducing the cost to transport itself. With the plant is dried, the major problem that will occurred if it is living, that is growth of mosquito’s pest, will be solved and also lead to a controlled, healthy and safe environment for living and for working.

1.3 Objectives

i) Investigate the biosorption of dyes by dried water hyacinth (DWH).
ii) Investigate the potential of dried water hyacinth as a low cost biosorbent.
iii) Identifying optimum condition in the removal of Methylene Blue (MB) dye ions by using dried water hyacinth.

1.4 Scope of study

This study investigates the biosorption abilities of dried water hyacinth (DWH) for the removal of Methylene Blue (MB) dye from aqueous solutions. There are four parameters to be studied which are the characteristic and effects of biosorbent dosage, initial concentration of MB, solution pH, and contact time.

1.5 Rational and Significant

Pollution caused by dyes had affected the society with serious environmental effect and health problems to human body. It is evident; therefore, removal of dyes from aqueous solutions is important. Problems caused by the rapid growth of water hyacinth in water sources can be solved by making use of the plant as a biosorbent to remove dyes. Also, water hyacinth is a low-cost, high efficiency of dye removal from dilute solutions and easily available material for adsorbent. Biosorption process is an effective alternative method to replace conventional method, which is high cost and more complicated compared to biosorption.

CHAPTER 2

LITERATURE REVIEW

2.1 Biosorption

2.1.1 Definition

Biosorption is a property of certain types of inactive, dead, microbial biomass to bind and concentrate heavy metals - or other types of molecules or ions - from even very dilute aqueous solution. Biomass exhibits this property, acting just as chemical substance, as an ion exchanger of biological origin. It is particularly the cell wall structure of certain algae, fungi and bacteria which was found responsible for this phenomenon. In similar meaning stated by D.J. Ju et al in his research, the uptake or accumulation of chemicals by biomass is known as biosorption. Opposite to biosorption is metabolically driven active bioaccumulation by living cells (Volesky, B. 2007). In that case, it takes a whole different approach for further exploration of the studies.

2.1.2 Biosorbent

There are a lot of efforts were made in many studies for the removal of dyes from either aqueous solutions or wastewaters. This includes the use of metal hydroxides, clays, sunflower stalks, bagasse pith, hardwood, fertilizers and steel wastes.

Suitable biomass comes as a waste material from fermentation industries or it is renewable, a certain abundant seaweeds growing in the oceans and ready to be collected. In either case, the costs of biomass raw materials are extremely low.

The use of microorganisms as biosorbents for dyes also offers a potential alternative to existing methods for detoxification. The cell wall of microorganisms, which consists essentially of various organic compounds such as chitin, lipids, amino acids and other cellular components, can provide a means for the passive uptake of reactive dyes (Z Aksu, 2001).

For example, as a basis for a metal biosorption processes, these biomass can accumulate in excess of approximately 25% of their dry weight in deposited heavy metals: Pb, Cd, U, Cu, Zn, even Cr and others. It is proven in many researches on biosorption which says that biosorption is sometimes a complex phenomenon where the metallic species could be deposited in the solid biosorbent through different sorption processes of ion exchange, complexation, chelation, microprecipitation, etc.

There are also new alternatives of suitable “formulated” biosorbents can be used in the process of metal removal and detoxification of industrial metal-bearing effluents. The most effective approach for the matter is the sorption packed-column configuration. It is stated that the recovery of the deposited metals from saturated biosorbent can be accomplished because they can often be easily released form the biosorbent in a concentrated wash solution which also regenerates the biosorbent for subsequent multiple reuse. This and extremely low cost of biosorbents makes the process highly economical and competitive particularly for environmental applications in detoxifying effluents of e.g.

- Metal-planting and metal-finishing operations,
- Mining and ore processing operations,
- Metal processing, battery and accumulator manufacturing operations,
- Thermal power generation (coal-fired plants in particular),
- Nuclear power generation, (etc.)

2.1.3 Biosorption Mechanism

In many researches, it is proven that the kinetics studies have been very helpful in the effort to determine the process of biosorption. There are several equations can be used and the results and graphs are almost all precise, understandable and always can be interpreted easily. But it is also important to determine the mechanism of sorption for design purposes. Based on the observation of bare eyes, it is considerably that in a solid-liquid biosorption process, the biosorbate (dye) transfer to the biosorbent (biomass) can be illustrated by either boundary layer diffusion (external mass transfer), intraparticle diffusion (mass transfer through the pores), or by both. Generally, the biosorption dynamics is accepted to consist of three consecutive steps:

i) Transport of biosorbate molecules from the bulk solution to the biosorbent external surface through the boundary layer diffusion.
ii) Diffusion of the biosorbate from the external surface into the pore of the biosorbent.
iii) Biosorption of the biosorbate on the active sites on the internal surface of the pores.

Usually, the last step, biosorption, is very rapid to be compare with the first two steps. For that reason, it can be considered that the overall rate of biosorption is controlled by either the boundary layer or pore diffusion, or combining both. According to D. Mohan et al in his study on 2004, it is proven that the boundary layer diffusion is the rate controlling step in systems characterized by dilute concentrations of biosorbate, poor mixing, and small particle size of biosorbent. Whereas the intraparticle diffusion controls the rate of biosorption in systems characterized by high concentrations of biosorbate, vigorous mixing, and large particle size of biosorbent. Also, in many studies, the results similarly showed that boundary layer diffusion is dominant at the beginning of biosorption during the initial removal, and then the rate of biosorption is regularly controlled by the intraparticle diffusion as the capacity of biosorbate has loaded the external surface of biosorbent.

The intraparticle diffusion parameter, *k*i (mg/g min0.5) is defined by the following equation (W.J. Weber Jr. et al., 1963):

$$q \qquad (2.1)$$

where q is the amount of MB adsorbed (mg/g) at time t, k_i the intraparticle diffusion constant (mg/g min$^{0.5}$), and c is the intercept. Theoretically, the plot of k_i versus $t^{0.5}$ should show at least four linear regions that represent boundary layer diffusion, followed by intraparticle diffusion in macro, meso, and micro pores (Y.S. Ho et al., 1998). These four regions are followed by a horizontal line representing the system at equilibrium.

2.1.4 Factors Affecting Biosorption

There are several factors that affecting the biosorption process. Studies have been done shows similar trends of results and observations for the same parameters investigated. Researches mostly investigate between these parameters to study its effect on biosorption process and how it can be improved to get the highest optimum uptake. This includes the biosorbent dosage, initial concentration of biosorbate, the solution pH, temperature, contact time between the sorbate and sorbent, particle sizes, and etc.

Generally, to explain the effect of biosorbent dosage, research on biosorption studies on Methylene Blue (MB) by tea waste done by M.T. Uddin et al., stated that the percentage removal of MB increased with the increase in adsorbent dosage. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase dosage of the adsorbent. But the adsorption density of MB decreased with increase in adsorbent dosage. Studies on other biomass such as guava leaf powder (V. Ponnusami et al., 2008), baggase (Raghuvanshi et al., 2004), papaya seed (B.H. Hameed, 2008) and fly ash (K. Rastogi et al., 2008) shows similar results.

As for the effect of time and initial concentration, it can be explained briefly in study done by Raghuvanshi et al., on baggase in 2004 which stated that the adsorption process was found to be very rapid initially, and a large fraction of the total concentration of dye was removed in the first 30 minutes. Though it was observed that adsorption of dye increased with an increase in dye concentration in the solution, which shows that removal of dye is dependent upon the concentration of dye solution. But as whole the percent removal decreases with the increase in dye concentration. Similar results have been obtained in research on other various biosorbent only the uptake value differs.

The effect of pH also shows similar results in research made by M. sarioglu et al., using biosolid, M.C. Ncibi et al., using *Posidonia oceanic*, B.H. Hameed et al., using pumpkin seed hull and many others using a varieties of biosorbent. Results obtained indicates that the effect of pH on the amount of dye removal was analyzed over the pH range from 2 to 10 and the pH 6 to 8 is usually the optimum pH for the removal process. This trend might be explained by in such pH, the biosorbent combines both negatively and positively charged cells surface, which enhance the electrostatic attraction between anionic and cationic species of both sorbate and biosorbent.

Temperature also affected the process of biosorption and it is proven by previous studies where the results shows that the dye uptake increasing with the increasing of temperature. It is clear that biosorption equilibrium is a thermo-dependent process. This effect may be due to the fact that at higher temperatures, an increase in the movement of solute occurs (M.C. Ncibi et al., 2007).

In this study, only four parameters are selected which is biosorbent dosage, initial concentration of biosorbate, solution pH and contact time.

2.2 Water Hyacinth

Figure 2.1 is a picture of water hyacinth (*Eichhornia crassipes*) taken at local pond in Pekan, Pahang. From the figure, it is clearly shown that this plant is freely available and abundant with no use for any reasons.